Colorado Department of Health

Radiation Control Division

Environmental Radiation Unit

Comments

on

DRAFT

WORKPLAN FOR

CONTROL OF RADIONUCLIDE LEVELS IN

WATER DISCHARGES FROM THE ROCKY FLATS PLANT

APRIL 5, 1991

I. Conclusion and recommendations.

As stated in Sections 3.3.3 and 3.3.4 (pp. 38-42), and Appendix II, the current Water Quality Control Commission standards for actinides can be expected to result in a 7% compliance failure rate for discharges of water from the Rocky Flats Plant into Walnut and Woman Creeks. Either or both of two changes to the pre-1989 operations at Rocky Flats may be sufficient to reduce that failure rate. They are (1) improved sensitivity and precision in measurement and (2) use of water purification techniques at the time of discharge. (The larger filter blocks that have already been installed may be expected to prevent actinide concentrations from exceeding Colorado Water Quality Control Commission standards **without further modifications to treatment procedures; the workplan should provide documentation of the resulting actinide levels.)**

Our understanding of the radiometric analysis procedures in use at the Rocky Flats Plant suggest some technological improvement could be implemented that would improve the sensitivity and precision of measurements. While it is true that a low-noise system with good detector geometry, such as the one employed by the Colorado Department of Health, can attain improved sensitivity and precision only by using larger sample volumes and extended data collection times, it should be recognized that many measurement systems are not low-noise systems A laboratory that does not employ a low-noise alpha spectrometry system can gain at least a five-fold improvement in sensitivity by acquiring one.

Demonstration of compliance, rather than compliance itself, seems to be the most difficult challenge presented by the Water Quality Commission's standards At the present time demonstration of compliance is a three-step process.

1. Accumulation of water in holding ponds prior to each discharge;
2. Analysis of water to test the performance of treatment filters prior to each discharge (with return of treated water to holding ponds), and

3 Evaluation of all analysis results prior to each discharge followed by a discharge/no-discharge decision

As stated in the Executive Summary (p viii), Sections 3 2 2 (pp 23-26), 3 2 4 Analytical Method Limitations (pp 31-32) and 4 1 8 Pond Water Discharge Plan/Item #2 (p 55), most analysis can be performed within 24 hours, provided sufficient resources are made available for rapid turnaround on occasions when that level of performance is requested of the laboratory Radiometric analysis requires a much longer time, regardless of the total resources provided, for thefollowing reasons:

1. Modern radiometric analysis is capable of measuring concentrations at the parts per trillion, quadrillion and quintillion, and in some cases at even lower concentrations.
2. Consistent with the current prevailing understanding of radiation hazards, existing standards for radionuclides are of the same order of magnitude and therefore require the best sensitivity that radiometric analysis can provide.
3. Such sensitive analysis necessarily requires elaborate and time-consuming sample preparation and measurement procedures.

Because completion of all analysis is now required before a discharge/no-discharge decision can be made, the decision relies on information about water in the holding ponds that grows obsolete with the passage of time; additional water flows into the holding ponds, or the water exchanges with the sediments in the holding ponds, or some other process causes the characteristics of the water in the holding ponds to change between the time of sample collection and the time that the discharge/no-discharge decision is made and executed. Always problematic is the question of what to do if analysis results fail to demonstrate compliance, or if the holding ponds overfill.

Rapid analysis of radionuclides at the targeted concentrations is not feasible, so it may be constructive to allow discharge before the radiometric measurements are completed, recognizing that the subject facility is responsible for compliance in any case. It may even be appropriate to develop a sampling plan, such as one using a continuous sampler, that would evaluate continuous treatment and discharge, as an alternative to the present sampling plan that treats each discharge as an isolated event

Notwithstanding the Running 30-day Averaging method, DOE should continue to seek new approaches or devise new methods to address the issues discussed in the preceding two paragraphs. The potential for future modifications or amendments to the workplan should be acknowledged

The discussion of Derived Concentration Guides (DCGs) in Section 3 3 4 (p 41) requires some modification for accuracy the DCGs in DOE Order 5400 5 are the average concentrations of each radionuclide in air or water that would yield a radiation dose of 100 $CEDE_{50}$ mrem/yr to Reference Man, assuming chronic, round-the-clock, non-occupationally-related consumption The use of the term "health-based" in this context is unclear

Concentrations that exceed the DCGs do not necessarily mean that the subject facility has failed to meet standards for protection against radiation, depending on the duration that high concentrations occur, and the average concentration over a year's time Similarly, concentrations that are well below the DCGs may result in a failure to meet standards for protection if other radionuclides are present, or if other pathways contribute to total dose, and the total dose to Reference Man would exceed 100 mrem/yr

By implementation of the Water Quality Control Commission's standards, which target concentrations far below the DCGs, a standard for protection considerably more stringent than 100 mrem/yr has been functionally adopted Under the circumstance, we do not see what place, if any a discussion of DCGs has in the workplan

The Water Quality Control Commission's standards are made even more stringent if they are interpreted as maximum values that may not be exceeded at any time, regardless of the time-weighted or flow-rate-weighted average concentrations over one year.

II. Specific comments regarding radionuclide sampling procedures

The Colorado Department of Health requires that split samples be archived for verification purposes, as required by the Agreement in Principle and the Interagency Agreement, to maintain accountability.

Our reading of Section 4.1.6 Using a 30-day Running Average (p. 51) indicates that the Water Quality Control Division will use 30-day moving averages to evaluate compliance. Since water may accumulate in the holding ponds for 30 days or more prior to discharge, and no more than a dozen discharge events are likely to occur in any year, the Radiation Control Division is unclear on how sampling will be conducted for calculating 30-day moving averages or how they will be used for evaluation. Please provide clarification of the procedures.

We recommend analysis of whole water rather than filtered or centrifuged samples, as described in Section 4.2.2 (p 57) We see no value in analysis of water by fractions, unless Rocky Flats Plant personnel require that type of information for internal process controls.

III Specific comments regarding analytical procedures

The formula for minimum detectable activity (MDA) in Section 3 2 4 Reporting Practices for Radiochemical Data (p. 27) is in error The formula employed by the Rocky Flats Plant laboratories for environmental measurements is

$$MDA = \frac{2.71 + (4.65\, s_B)}{T_s \quad Eff \quad Y \quad a \quad V}$$

where

s_B = $\sqrt{\text{blank counts}}$ (or, more appropriately, $\sqrt{\text{blank count rate } T_s}$);

Note: *The Rocky Flats Plant laboratories actually use a much more elaborate method of computing s_B than this. If additional detail is required, please consult EG&G personnel.*

T_s = sample count time (sample measurement time);

Eff = detector efficiency (usually overall detector efficiency for a given sample configuration, rather than absolute efficiency with adjustments), with units of counts/disintegrations;

Y = chemical recovery;

a = conversion factor (e.g., 2.22 dpm/pCi);

and V = sample volume.

Because the workplan describes the terms, formulas and procedures employed at the Rocky Flats Plant, the information in the workplan should be reconciled with the information given above.

The Radiation Control Division prefers to use the notation LLD, for Lower Limit of Detection. MDA has been used to describe different formulas for calculating detection limits of various types in past years.

The coefficients, 4.65 and 2.71, in the formulas above provide an LLD (or MDA) at the 95% confidence level. It is important to keep in mind that, at the LLD, the confidence interval is approximately equal to 100% of the measured value. (This would be a true confidence level.) Other definitions of detection limits, such as the one employed by the U. S EPA for its National Interim Primary Drinking Water Regulations, set the detection limit as the concentration at which the 95% confidence interval on the measurement would be exactly equal to the measured value.

It is suggested in Section 3 2 4 Reporting Practices for Radiochemical Data (p 28) that it is advantageous to report all measurements, whether or not they fall below the LLD (or MDA), with an attempt to justify this point of view The Radiation Control Division will not endorse such a statement and we hope that it will be modified in some way so that it will not be interpreted as a universally accepted opinion

We disagree with the statement in Section 4 1 7 (p 54), "The reported MDA should be interpreted as that of the process and not that of a single measurement ." The Colorado Department of Health's approach to environmental actinide analysis is not process-oriented Instead we are highly opportunistic in short-run uses of extended sample volumes and measurement times, particularly when chemical recoveries are high enough to warrant expenditure of resources to improve sensitivity

Furthermore, a rated detection limit should not be used for any measurement that fails to achieve the stated degree of sensitivity Since the range of sensitivities that we regularly achieve is so large, it's only practical to calculate a unique LLD for each sample The primary objective of the Radiation Control Division's surveillance program is vicinity characterization rather than determination of compliance, pushing the sensitivity of the measurements in order to routinely quantify the contribution of fallout to background is a necessary goal for our program

With regard to another statement in Section 3 2 4 Reporting Practices for Radiochemical Data (p.27), and a statement in Section 4 3 (p 59), accuracy is achieved through sensitivity, precision, specificity and reproducibility. Bias is ordinarily introduced when the analysis technique lacks adequate specificity, but may be subject to other parameters that affect the overall validity of a measurement technique.

We disagree with all three highlighted conclusions that are listed in Section 3 3.2 (p. 35) and discussed throughout Sections 3 3.2 (pp 35-37), 3.3.3 (pp 37-40), and 3.3.4 (pp 41-42), and in Appendix II. The sensitivity and number of measurements shown in Tables 3.2, 3.3 and 3.4 (p. 36) are not extraordinary, and most importantly variances, standard deviations or some other measure of variability, or p-values, are not present to support the conclusions. While averages may be of interest, no discussion defines the usefulness of the information. Ranges and quartiles may better help to evaluate the need for treatment prior to discharge or for improvements to existing treatment

The reference to Section 3.3 3 (p. 39) to "analyses conducted near .. MDA" is unacceptable, reported averages in Table 3.6 (p 39) and 3 7 (p 40) are about 40 times lower than the MDAs reported in Section 3 2 4 Reporting Practices for Analytical Data (p 28) and about 10 times lower that the MDAs reported in Table 3 1 (p 29) The reported average americium concentrations in Table 3 7 (p 40) are at least as high as the reported plutonium concentrations in Table 3.6 (p 39) If the implied ratios are not to be believed, and they are not, then the statistical evaluation is flawed Similarly, if the numbers of measurements and the statistical procedures are adequate, then Tables 3 6, 3.7 and 3.8 (pp. 39-41) should not be littered with reported averages concentrations that are less than zero

The statements about replicate analysis and improved sensitivity in section 4 0 Workplan Issues (p 47) indicate a failure to understand the fundamental techniques of analytical chemistry Replicating analysis will not improve sensitivity, it only provides a duplicate of an insensitive analysis Cross-contamination and laboratory errors do not increase with improving sensitivity, increasing sample volumes, replicate analysis or increasing data collection times

The need for extreme sensitivity appears to be forgotten in the Section 4 0 Workplan Issues (p 47) discussion of ambient concentration characterization The Rocky Flats Plant's current measurement techniques and statistical analysis are inadequate to characterize ambient actinide concentration either on-site or off-site and would not be able to attribute any significance to the findings that are sought in Section 4 2 (p 56)

In light of this review the statement in Section 3 2 4 Analytical Method Limitations (p 30) should be corrected to read, "The accuracy and reliability of routine plutonium and americium data that are produced by the Rocky Flats Plant laboratories below this value are questionable," or the statement should be omitted entirely The statement is repeated in Section 4 0 Workplan Issues (pp 46-47) and should be modified accordingly

The statistical evaluation in Sections 3 3 2, 3 3 3 and 3 3 4 (pp 35-42) and Appendix II, together with the conclusions that have been drawn in other parts of the workplan, quite obviously rely exclusively on measurements that have been reported without regard to lower limits of detection Since the workplan places so much reliance on such information it is difficult to understand what place any discussion of detection limits has in the workplan or what value is placed on them

Figures 3,1 (p 24) and 3 2 (p. 25), and the narrative in Sections 3 2 7 (p 33) and 4.1.6 Single Sample Exceedences (pp 51-52) do not describe any attempt to reconcile the first and subsequent analysis results when adverse information is obtained. When anomalous analysis results are obtained it is a generally accepted practice to recheck and verify data However, if the Rocky Flats Plant's General Radiochemistry and Routine Analytical Services Protocol, GRRASP 9/14/90 Rev. 1.1, referenced in Section 3 2.4 Analytical Method Limitations (p 31) is to be believed, then the probability of sampling or analysis error is infinitesimal, all reported results would be valid on the first pass without need for verification. Anomalous information that is adverse should be expected to occur with the same frequency as anomalous information that is not; anomalous results must not, repeat not, be defined simply as any adverse information It must also be pointed out that it is an unacceptable practice to keep resampling and reanalyzing until a desirable result is obtained, unless there is a justifiable rationale for doing so

Section 3 3 3 (pp 37-41), titled "Assessment RFP Water vs CWQCC Stream Standards, " repeats conclusion drawn in Section 3 3 2 and compares average measured plutonium concentrations in community water supplies with the Water Quality Control Commission's surface water standards in Tables 3.6, 3 7 and 3 8 (pp 39-41) It may be useful to construct this section so that it provides the information referenced in the title

The section on analytical quality control, Section 4 1 7 (p 54), is surprisingly short Where it is stated that "Quality control checks of analytical methodology will " does it mean that the method must be validated repeatedly?

With regard to the standardized methods cited in Section 3 2 4 Analytical Method Limitations (pp 30-31), 4 3 (pp 58-59), and 4 3 1 (pp 59-60), the Radiation Control Division does not advocate strict adherence to standardized methods Such a practice will in the long run inhibit improvements to analytical procedures The method numbers cited twice in Sections 3 2 4 Analytical Method Limitations (p 30) and 4 3 1 (pp 59-60) are irrelevant to this workplan

IV Specific comments regarding treatment technologies

Considering the inadequacy of measurement techniques employed by the Rocky Flats Plant, evaluations of the treatment technologies described in the Executive Summary (p ix), Section 3 4 (pp 42-45), and all parts of Section 4 (pp 46-65) are not expected to provide accurate information if treatment technologies are tested in situ or if bench-scale testing of treatment technologies at Rocky Flats evaluates removal of material in the relevant range of concentrations

Uranium, which may present hazards to researchers, would be no better an indicator of removal efficiency than iron or sulfate Uranium, nor iron or sulfate, are acceptable substitutes for plutonium or americium in the analysis of chemical treatment technologies due to dissimilar chemical properties

The conclusions presented in Section 3.4 1 Sample Filtration/Filter Bag Evaluations (pp 42-43) conflict with those presented in Section 3.4.2 Speciation and Low-Detection-Limit Study (p. 45). In the first case a study of a particle-size filtration system failed to provide conclusive results, probably due to inadequate sensitivity and precision in the measurements. In the second case an LANL study of a particle-size filtration system did provide conclusive results. Assuming that LANL can reliably measure concentrations of plutonium and americium in the relevant range, the results of the LANL project can be taken at face value and agree with expectations.

V Miscellaneous items

Section 2.4 1 (p. 11) states that Walnut Creek flows "offsite through a diversion ditch bypassing Great Western Reservoir" Walnut Creek flows off the property, Broomfield Diversion Ditch begins east of Indiana Street.

Section 3.2 6 (p 33) states that the Broomfield Diversion Ditch "is not tributary to Walnut Creek ." In fact, the Broomfield Diversion Ditch does feed Walnut Creek Dry Creek Valley Ditch and Walnut Creek run together for some distance in the original Walnut Creek stream bed, then split Flow to the two streams is monitored and controlled by the City of Broomfield personnel

Section 4 0 Workplan Issues (p 47) states, "Only by comparison to ambient levels in local areas removed from potentially impacted zones can the need for action be established " While we agree that contaminant concentrations that are attributable to worldwide fallout are a likely endpoint for remedial activity, it must be remembered that substantially all of the transuranics in the Rocky Flats Plant vicinity originated from Plant operations

From our reading of Sections 3 4 1 (p 42) and 4 4 1 Speciation and Quantitation of Radiochemical Species (p 62), it appears that the authors of the workplan are not aware of the work of Jess Cleveland, Terry Rees and others Dr Cleveland is currently at USGS/Denver Federal Center Previously he worked for Dow Chemical/Rocky Flats This group has provided a large body of site-specific information about actinides in the environment at Rocky Flats The discussion provides no insight into how the information will be used in the context of the Interagency Agreement (IAG), but certainly a literature search is indicated and may save duplication of effort